Degradation Behaviour of Flame Retarded HIPS

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Introduction

Brominated flame retardant containing plastics are widely used for electric equipments, such as casings for computers, refrigerators, TV sets, etc, in order to reduce the risk and damage of flame. However, hazardous brominated compounds, such as brominated dioxins and furans, are released into the environment during flame or end-of-live treatments, such as combustion and recycling. These compounds are accumulated in fatty tissues, causing a higher risk of developing cancer. As a consequence, i.e. the EU enacted the directive 2002/95/EC (RoHS), which prohibits the use of polybrominated biphenyls and diphenylethers in electric and electronic equipments. However, since old electric household appliances might still contain polybrominated diphenylethers and other brominated compounds as flame retardants, a processing method for the removal of these harmful compounds from waste plastics is required. Plastics can be converted into liquid and gaseous fuels by pyrolytic processes, or energy can be obtained from their combustion. In any case, HBr and brominated organic compounds are released, being hazardous to environment and health as well as corrosive, endangering the processing facilities themselves. Additional, Sb_2O_3 is frequently added as a synergist, having a considerable impact on the formation of brominated products and the degradation of the polymer itself. Therefore, it is necessary to understand the processes, accompanying the thermal decomposition of these flame retarded plastics.

Brominated flame retardants are mainly used to improve the flame retardancy of casings made for TV sets and computers. The effect of tetrabromobisphenol-A on the thermal degradation of printed circuit boards was reported earlier (Grause et al. 2008). In this paper, the effect of decabromodiphenylether (DPE) and decabromodibenzyl (DDB) (Fig. 1) on the thermal degradation of high impact polystyrene (HIPS) was investigated in the presence and absence of Sb_2O_3.
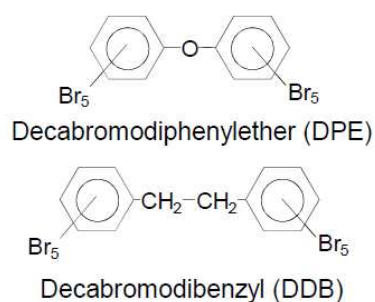

Fig.1. Flame retardants used in these experiments

Materials and Methods

For these experiments, HIPS was blended with DPE and DDB, respectively. Sb_2O_3 was also added to some samples. The composition of the samples used is shown in Table 1.

Table 1 Sample composition

Sample	Flame retardant	Synergist
DPE-Sb(0)	DPE 13 wt%	—
DPE-Sb(5)	DPE 13 wt%	Sb_2O_3 5 wt%
DDB-Sb(0)	DDB 13 wt%	—
DDB-Sb(5)	DDB 13 wt%	Sb_2O_3 5 wt%
HIPS	—	—

The TGA measurement was performed with a Seiko TG/TDA6200 over a temperature range of between 50 and 700°C at a heating rate of 5 K min^{-1}, using 10 mg of sample. The helium flow was set to 200 ml min^{-1} in order to avoid corrosion, caused by the diffusion of HBr, released during the decomposition of flame retarded

HIPS. The measurement was controlled by a Muse Measurement 4.1 software.

Pyrolysis experiments took place in a quartz glass reactor, using 500 mg of sample. The same conditions were used as for the TGA-experiments. The product oil was qualitatively analyzed by GC/MS (HP6890/HP5973) and quantified by GC-FID (GL Science GC390). Brominated compounds were analyzed by GC-ECD (HP6890). The same type of column (GL Science Inert Cap 5MS/Sil) was used for all analyzes.

Results and Discussion

The thermal degradation of HIPS and DPE-Sb(0) started at about 300 °C at a heating rate of 5 K min^{-1} (Fig. 2). While HIPS degraded in one step, a shoulder attached to the main degradation step was observed for DPE-Sb(0). The degradation of DPE-Sb(5) started at about the same temperature as HIPS, accelerated, however, strongly, resulting in a early maximum at 330 °C and a second maximum at about 400 °C, which might be identical to the DPE-Sb(0) degradation. It is obviously that besides an accelerated degradation of the flame retardant, the presence of Sb$_2$O$_3$ has also a major impact on the HIPS degradation, resulting in the degradation of the polymer at a lower temperature. A closer look at the degradation of DPE-Sb(5) at a heating rate of 5 K min^{-1} by TG-MS reveals that styrene and its dimer and trimer were produced during both stages of the degradation. Hydrogen bromide, however, was only released during the first stage of the degradation. Obviously, the addition of Sb$_2$O$_3$ triggered the decomposition of the flame retardant at a lower temperature, releasing high concentrations of HBr. HBr underwent a reaction with Sb$_2$O$_3$ under the formation of SbBr$_3$ and water (Jakab et al. 2003). The degradation of the

Fig.2. TGA/DTG of HIPS and flame retarded HIPS

Fig.3. TGA and TG-MS of DPE-Sb(5)

flame retardant itself is a radical reaction causing the formation of bromine radicals in high concentrations. The radical transfer to the polystyrene chain resulted in HBr and a polystyrene macroradical, which underwent chain fission and the subsequent release of styrene by a zipper mechanism from the radical bearing chain. The other chain fragment has an unsaturated chain end, being the source of the increased production of by-products.

The degradation of HIPS resulted mainly in styrene and its dimers and trimers (Fig. 4). The addition of the flame retardant had several effects on the product distribution, while the addition of Sb$_2$O$_3$ did not change the product distribution significantly. First, the number of products increased in the presence of the flame retardant. While in the absence of the flame retardant only styrene and its oligomers were
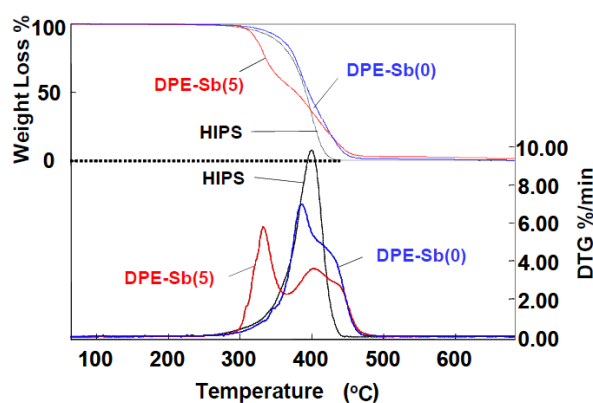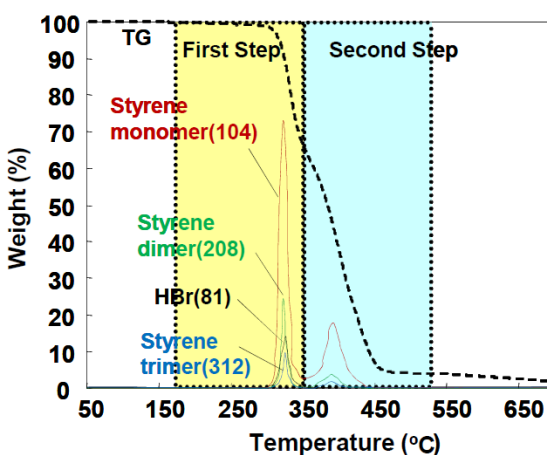
observed, after the addition of the flame retardant, products occurred, which were not related to the zipper mechanism or the back-biting mechanism in general responsible for the decomposition of polystyrene. These newly derived products were formed by the strong impact of bromine radicals. Second, the amount of dimers and trimers increased compared to the amount of styrene. This indicates that the relevance of back-biting processes increased, while less styrene was formed by the zipper mechanism.

GC-ECD revealed the presence of various brominated organic compounds present in the product oil of the thermal degradation of flame retarded HIPS (Fig. 5.). DPE released more brominated compounds in the presence of Sb_2O_3 than in its absence. When DDB was used as a flame retardant, the vice versa effect was observed. According the different structures of the flame retardants used, the chromatograms showed significant differences. While DPE formed brominated phenols and dibenzofurans, brominated phenanthrenes were observed from the degradation of DDB. α-Ethylbenzene, however, was found as a product of both DPE and DDB containing HIPS, since it is not derived directly from the decomposition of a flame retardant, but resulted from the reaction of HBr with styrene.

The pathway of the degradation of flame retarded HIPS differs strongly from that of flame retarded free HIPS (Fig. 6). In the absence of a flame retardant, HIPS undergoes a chain fission in a first step, following the unzip-mechanism as the main reaction pathway (Levine and Broadbelt 2008, Polce et al. 2008). To some extent, back-biting reactions take place, resulting in dimers and trimers. In the presence of a flame retardant, the mechanism changes due to the high concentration of free bromine radicals. After the degradation of the flame retardant molecule, the resulting bromine radicals transfer the radical to the polymer chain, forming HBr. Since the secondary macroradical is more stable than the primary one, it can be assumed that solely the secondary macroradical is formed, which can decompose by the unzip-mechanism. The other side of the chain is stabilized as an alkene and does not undergo a further degradation until another radical transfer takes place. Each radical transfer leaves an odd chain end, which results in products different to those obtained from the degradation of pure HIPS.
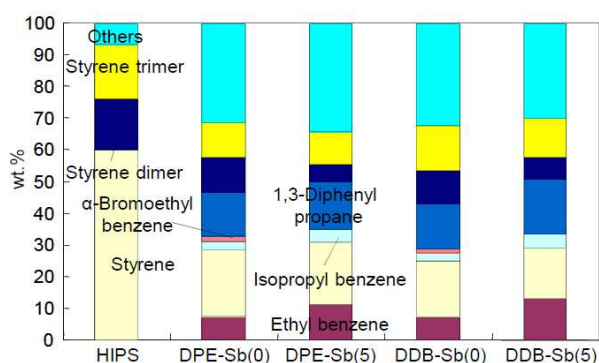

Fig.4. Product distribution of the degradation of flame retarded HIPS (identified organic products)
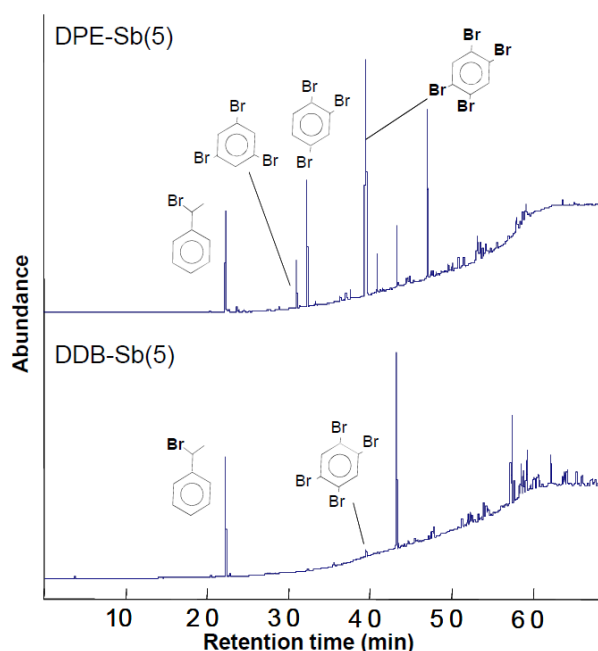

Fig.5. GC-ECD of the degradation products of flame retarded HIPS containing Sb_2O_3
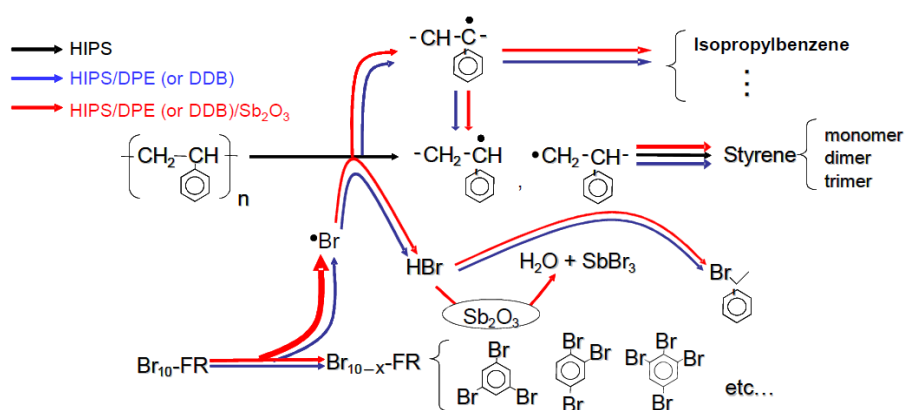
Fig.6. Degradation pathway of HIPS and flame retarded HIPS

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